

**ON MARTIAN ALTERATION AS A FUNCTION OF CLIMATE AND VOLCANISM.** W. Ian Ridley and Geoffrey S. Plumlee, U.S. Geological Survey, Box 25046, Denver, CO 80225, USA.

**An Early Warm, Wet Climate:** Assuming an atmospheric  $p\text{CO}_2$  between 10 and 2 bar, the initial pH of Martian rainwater would lie between 3.45 and 3.75 at 25°C with  $\text{CO}_2$  (aq) between 0.33 and 0.017 moles/kg. Assuming a veneer of basalt of Chassigny-parent composition, then fluid-rock alteration under these fluid pH conditions (and any  $\text{pH} < 5$ ) would initially produce an alteration assemblage of Fe-smectite (+/- ferrihydrite), Mn-hydroxide, kaolinite, apatite and chalcedony. The fluid pH would rise and above  $\text{pH} \sim 5$  the alteration assemblage would include dolomite, calcite, K-feldspar, and dawsonite  $\text{NaAlCO}_3(\text{OH})_2$ . The effect of lower pH and higher  $\text{CO}_2$ (aq), i.e., for atmospheric conditions at the high end of  $p\text{CO}_2$ , the alteration effects are: (1) to cause more rock to be altered per mass of rainwater; (2) to decrease the rate of pH rise for each rock increment altered; (3) to cause more carbonates and hydrated carbonates to form at  $\text{pH} > 5$ .

Extensive and intensive volcanism would result in acid rain which would have been an important component of surface alteration. Assuming a volcanic gas composition similar to emanations at Kilauea, then addition of 0.1 grams of gas per kilogram of rainwater would reduce the fluid pH by at least 1 log unit, and add  $\text{SO}_4$ (aq) and  $\text{Cl}$ (aq) to the fluid. The resulting rock alteration would be similar, but substantially more extensive, to that for rainwater, and provide increased proportions of carbonate, hydrous carbonate and gypsum. Another important consequence of volcanism would be the development of volcanic-hydrothermal systems. Acid volcanic gas condensates would alter basaltic rocks in and around volcanic conduits to produce zoned silica-alunite-anhydrite-hematite-nontronite-smectite-carbonate assemblages. Large-scale hydrothermal systems circulating within volcanoes would alter basaltic volcanics to quartz-pyrite-carbonate-epidote-albite alteration assemblages.

**Climate Change to Drier, Cooler Regimes:** Gradual change of climate would result in either evaporation and/or freezing of previously stable hydrous fluids. Hydrothermal fluids that mixed with permafrost meltwaters (probably produced by impact) were likely acidic ( $\text{pH} 3\text{--}5$ ) and saline, and would produce alteration assemblages of nontronite-anhydrite-kalonite-Mg-smectites-Mg-chlorites-quartz. Near surface quenching of hydrothermal outflows from impact- and volcanic-hydrothermal systems would produce extensive silica- and/or carbonate-rich precipitates similar to terrestrial sinter and travertine terraces. Evaporation (up to 99.7%) of waters that had previously reacted with Fe-rich basalts would produce gypsum, dawsonite, dolomite, Na- and K-feldspars and phosphate minerals. More extensive evaporation ( $> 99.7\%$ ) would add K- and Mg-sulfates and  $\text{MgOHCl}$ . However, it is unlikely that either NaCl or KCl would precipitate during evaporation.

The weathering of basalt at 0.1°C buffered by the present Martian atmosphere would produce assemblages containing hematite/goethite (or ferrihydrite), gibbsite, kaolinite, chalcedony, smectites (Ca-, Mg-nontronites), heulandite, Mg-silicates, K-feldspar, trona,  $\text{MgOHCl}$ , dolomite, and arcanite (K-sulfate). Cooling of the resulting brines (probably not colder than -1°C) to near the eutectic temperature would produce ice (or clathrates), chalcedony, arcanite, dolomite, Mg-silicates, and epsomite (Mg-sulfate). Thus, reaction of groundwaters with basalt and the subsequent freezing of the fluids would produce a high-sulfur, low-chloride mineral assemblage which might form an important component of the modern regolith.

Note: These predictions are based on reaction geochemical path models using CHILLER and GEOCHEMISTS WORKBENCH™.